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BUREAU OF CHEMISTRY—BULLETIN No. 92.

H. W. WILEY, Chief.

THE EFFECT OF WATER ON ROCK POWDERS.

BY

ALLERTON S. CUSHMAN,

CHEMIST, DIVISION OF TESTS.

WASHINGTON:

GOVERNMENT PRINTING OFFICE.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Chemistry,
Washington, D. C., March 3, 1905.

Sir: I beg to transmit herewith for your inspection and approval the manuscript containing the data secured in the study of the effects of water on rock powders, and to ask that it be printed as Bulletin 92 of this Bureau. This manuscript contains data of great practical interest in connection with the selection and treatment of materials for road building. It also presents facts of practical application respecting the chemical reactions which go on in finely ground material derived from rocks and certain artificial products. The illustrations are necessary to the proper elucidation of the text.

Respectfully,

H. W. Wiley, *Chief.*

Hon. James Wilson,
Secretary of Agriculture.

CONTENTS.

	Page.
Wet grinding	5
Marked effect of water upon the binding power of certain substances	7
Discussion of phenolphthalein reaction	9
The colloid theory	12
Absorption power of clays and rock powders	16
Practical applications	22
Summary	23

ILLUSTRATIONS.

		Page.
PLATE I.	Fig. 1.—Orthoclase ground *dry* in a ball mill for three hours. Fig. 2.—Orthoclase ground *wet* in a ball mill for three hours	8
II.	Fig. 1.—Orthoclase ground wet in an agate mill for three hours. Fig. 2.—Wet ground orthoclase stained with methylene blue	8
III.	Fig. 1.—Orthoclase dust in the finest state of subdivision possible. Fig. 2.—Same powder as shown in fig. 1, ground wet, dried, and repulverized	16
IV.	Fig. 1.—Same powder as shown in Plate III, fig. 2, but stained with methylene blue. Fig. 2.—Wet ground orthoclase powder remaining in suspension in water after several days, dried, and lightly pulverized	16

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THE EFFECT OF WATER ON ROCK POWDERS.

WET GRINDING.

It has been known for a long time that when certain finely powdered minerals are treated with water, reactions take place which result in partial decomposition and solution. Probably the earliest experimenters to call attention to this action were W. B. and R. E. Rogers, who first published a note on the subject in 1848.[a] More recently Daubree[b] has given much attention to the subject. In one experiment he made fragments of granite and quartz slide over each other in a hollow cylinder partially filled with water and rotating on its axis. The fragments rounded in the cylinder could not be distinguished either in form or general aspect from the natural detritus of a river bed. A second product was an extremely fine impalpable mud, which remained suspended in the water several days. During the production of this fine sediment the water, even though cold, was found in a day or two to have acted chemically upon the granite fragments and yielded a considerable quantity of soluble salts, *consisting chiefly of silicate of potash*. A third product was an extremely fine angular sand, consisting almost wholly of quartz, with scarcely any feldspar, nearly the whole of the latter mineral having passed into the state of clay. Still more recently Clarke[c] noted that the immediate action of water on many minerals could be shown by the alkaline reaction obtained with phenolphthalein indicator.

For several years investigations have been carried on in the Division of Tests, Bureau of Chemistry, on the effect of water on the binding power of rock dusts, more particularly in its relation to certain important road-building problems. The results of these investigations, which have been given out from time to time in various publications,[d] pointed to the fact that water produced a colloid or glue-like surface condition of the particles, leading to plasticity in the wet mass and binding power on induration. It has already been shown that most

[a] Amer, J. Sci., 2d series, **5**: 401.

[b] Geike, Geology, 3d ed., p. 385.

[c] U. S. Geological Survey Bul. No. 167, p. 156.

[d] U. S. Dept. Agr., Bureau of Chemistry, Buls. Nos. 79, 85, and Circular No. 17; J. Amer. Chem. Soc., **25** : 5; also Trans. Amer. Ceramic Soc., **6** : 3.

rock powders when mixed with water to the consistency of a stiff dough and allowed to stand, gradually increase in binding power up to a maximum constant value which is generally reached at the end of twenty-four hours. If, however, this same wet mass is worked or kneaded by hand the binding power rises to a much higher value. These results are easily explainable if we suppose that the action of the water takes place upon the surface of the particles, which soon becomes clogged with the product of the hydrolytic decomposition. A similar case is presented by finely divided metallic lead, which is readily attacked by water at first, the reaction slowing down as the particles film over with hydroxid and carbonate.

Following up these results, Mr. L. W. Page conducted a series of experiments in which kilogram charges of rock dust were ground with approximately 20 per cent by weight of water in the ball mill for about three hours. At the end of this time the binding power was determined by test and compared with the binding power as obtained in the ordinary way, where the rock dust was ground dry for three hours, mixed with water to a stiff dough, and allowed to stand for twenty-four hours. Almost without exception the binding power has been increased very much by this method of procedure, as is shown in Table I. It has also been found that, having once been developed by wet grinding, the higher cementing value is not destroyed by subsequent air drying—a most important point from the road-building point of view.

TABLE I.—*The relative cementing value of various rock samples when ground wet and dry.*

Serial No.	Kind of rock.	Cementing value.			Color with phenolphthalein cold.
		Dry grinding.	Wet grinding.	Difference.	
393	Chert	6	23	17	No color.
756	Dolomite	28	31	3	Decided pink.
841	Diabase	15	121	106	Pink.
858	Quartzite	1	31	30	No color.
865	Granite	13	15	2	Do.
936	Sandstone	25	78	53	Faint pink.
977	Limestone	9	28	19	Decided pink.
980	Basalt	128	500	372	Very pink.
986	.....do	12	125	103	Decided pink.
987	.....do	15	25	10	Faint color.
988	.....do	21	421	400	Decided pink.
999	Eclogite	15	130	120	Pink.
1003	Sandstone	61	174	113	Do.
1005	Feldspathic sandstone	10	35	25	Do.
1006	Chert	7	18	11	No color.
1008	Gneissoid granite	1	35	34	Faint pink.
1009	Dolomite	32	174	142	Decided pink.
1010	Slate	14	43	29	Faint pink.
1011	Gneiss	2	52	50	Do.
1012	Epidosite	12	83	71	Pink.
1015	Dolomite	13	43	30	Decided pink.
1016	Chert	1	22	21	Faint color.
1017	Hornblende granite	1	29	28	Do.
1018	Quartzite breccia	1	13	12	No color.
1019	Granite	1	53	52	Do.
1020	Arposic gneiss	4	33	29	Faint pink.
1021	Granite	1	25	24	Pink.
1022	Altered peridosite	14	30	16	Faint pink.
1023	Altered diabase	8	208	200	Decided pink.
1024	.....do	10	75	65	Do.
1025	Feldspathic basalt	108	162	54	Pink.

TABLE I.—*The relative cementing value of various rock samples, etc.*—Continued.

Serial No.	Kind of rock.	Cementing value.			Color with phenolphthalein cold.
		Dry grinding.	Wet grinding.	Difference.	
1026	Banded chert	1	12	11	No color.
1027	Chert	12	106	94	Decided pink.
1028	Arkose	17	200	183	Do.
1032	Limestone	5	79	74	Do.
1037	Argillite (slate)	29	179	150	Do.
1038	Limestone	14	113	99	Do.
1040	Altered diabase	11	27	16	Do.
1042	Diabase	2	101	99	Pink.
1044	.....do	8	95	87	Do.
1061	.....do	5	58	53	Faint pink.
1072	Limestone	38	97	59	Decided pink.
1074	Sandstone	12	34	22	Faint pink.
1075	Slate	7	25	18	No color.
1076	Dolomite	5	48	43	Distinct pink.
1077	Dolomitic limestone	2	18	16	Dark pink.
1079	Syenite	5	20	15	No color.
1080	Dolomitic limestone	6	55	49	Decided pink.
1081	Limestone	17	55	38	Do.

MARKED EFFECT OF WATER UPON THE BINDING POWER OF CERTAIN SUBSTANCES.

In some of the earlier investigations conducted in this laboratory a number of experiments had been made on powdered glass, which was found to have little or no binding power, even if prepared in the finest state of subdivision by dry grinding and elutriation. When, however, following up the results on rock powders, plate glass was ground wet in the ball mill, the surprising fact was established that a very high binding power had been developed, so high, indeed, that briquettes made from this glass powder became so hard that they could not be broken in the hands or indented by the finger nail. It is a matter of common knowledge that glass, even in the form of glass vessels, is acted upon by water. In a powdered condition this action would, of course, go farther, but under the influence of wet grinding, in which the products of the reactions were continually being worn off of the surfaces of the particles, it was presumable that a sufficient amount of sodic silicate had been formed to cement the coarser particles together. This was manifestly a point which could be very simply investigated. Phenolphthalein showed an immediate slight alkaline reaction on moistening glass which had been ground dry, but a deep and strong reaction with glass that had been ground wet. Two hundred grams of glass that had been ground wet were thrown on a large double filter and extracted with several liters of hot water. The filtrates were evaporated in platinum and weighed. More than 10 grams (5 per cent) of a hard, glue-like residue were obtained which was without doubt mainly sodic silicate. When this residue was obtained there could be no longer any question as to the reason for the binding power of wet-ground glass powder, the glue-like nature of sodic silicate solutions being too well known to require discussion. The inter-

esting point was whether the increased binding power of ordinary rock dusts was due to analogous if not similar causes.

Before describing further experimental work it will be necessary to present some of the physical-chemical theories, which are advanced to account for the constitution and structure of all substances formed from an originally fluid or molten condition. To quote Van't Hoff:[a]

> We are certainly entitled to speak of solid solution in certain definite cases, where the complete homogeneity combined with the possibility of varying composition, which are characteristic of the state of solution, are found. In colored specimens of glass and in isomorphous mixtures—of two alums, for example—we are just as little able, even with the help of the microscope, to perceive the presence of more than one substance, as in a solution of sugar in water. It is a familiar fact that the ordinary colorless alum, when crystallizing from solutions containing the highly colored chrom-alum, forms octahedra more or less tinted with chrom-alum; and yet the most minute observation reveals no gross irregularities in the physical distribution of the material, or any other evidence of lack of homogeneity. In such a case, therefore, we speak of the existence of a solid solution. When the substance is amorphous, as in the case of colored glass, the analogy to a fluid is so complete that the two are connected by a series of more or less viscous mixtures in such a way that no sharp distinction can be drawn. Of course, when the solid solution is crystalline it must be admitted that it differs from a fluid solution fundamentally, in so far that an arrangement of the molecules according to some definite order has taken place. The essential point is that the laws of fluid solutions have been successfully applied to solid ones.

In accordance with these ideas it is now held that glass is a homogeneous solid solution of lime, silica, and the alkalis, or better, perhaps, of an alkaline silicate in a calcium silicate in which no crystalline aggregates form as the orginal fluid mass cools. The constitution of igneous rocks is explained by considering that from the original molten magma crystalline aggregates, such as feldspar, mica, augite, etc., separate at different temperatures on cooling, though these may be more or less modified by substances retained in solution. In addition to the crystalline constituents, glass-like amorphous bodies occur, which are in the nature of true solid solutions.

As a result of Richardson's[b] brilliant researches into the constitution of Portland cement, we now know that hydraulic cements consist of solid solutions of certain calcic aluminates in certain calcic silicates. These are formed by the more or less rapid cooling of the cement clinker, which results from heating the proper mixture of lime, alumina, and silica to a point where diffusion is complete among these constituents. The essential characteristic of such a cement is that when ground to a fine powder and treated with water certain reactions take place at once, which lead in the case of Portland cement to a hydraulic set, that is to say, the cement sets to a solid stone-like mass under

[a] Decennial Publications Univ. of Chicago, 2d series, 18 : 59. "Physical chemistry in the service of the sciences."

[b] Cement, 5 : 3, et seq.

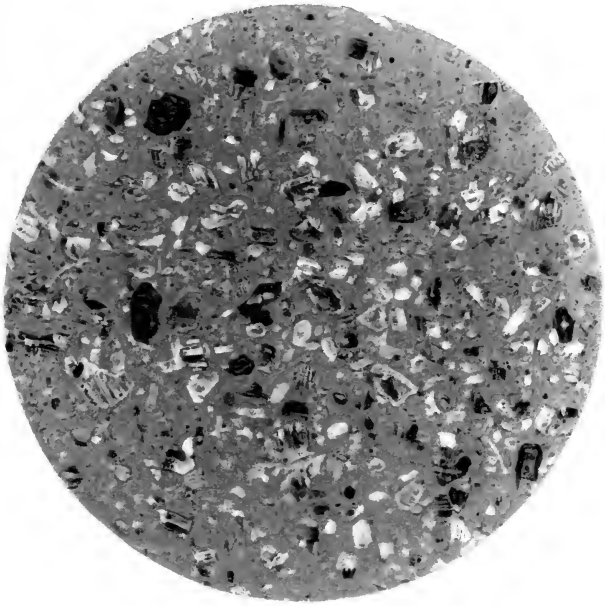

FIG. 1.—ORTHOCLASE ROCK GROUND DRY IN A BALL MILL FOR THREE HOURS.

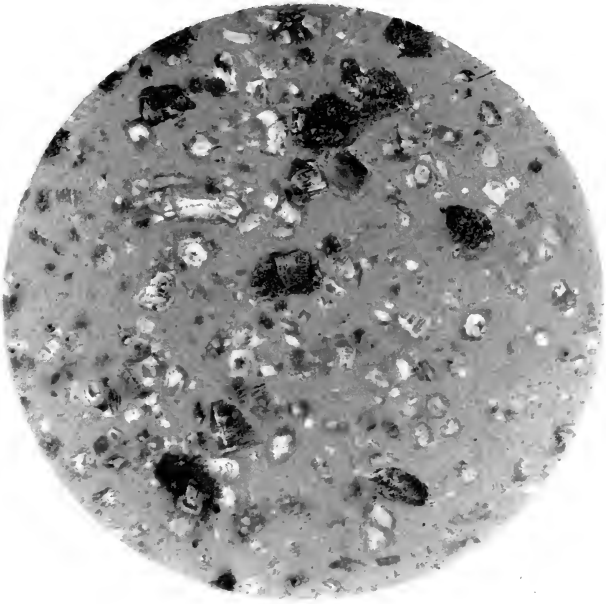

FIG. 2.—ORTHOCLASE ROCK GROUND WET IN A BALL MILL FOR THREE HOURS (ENLARGED 25 DIAMETERS).

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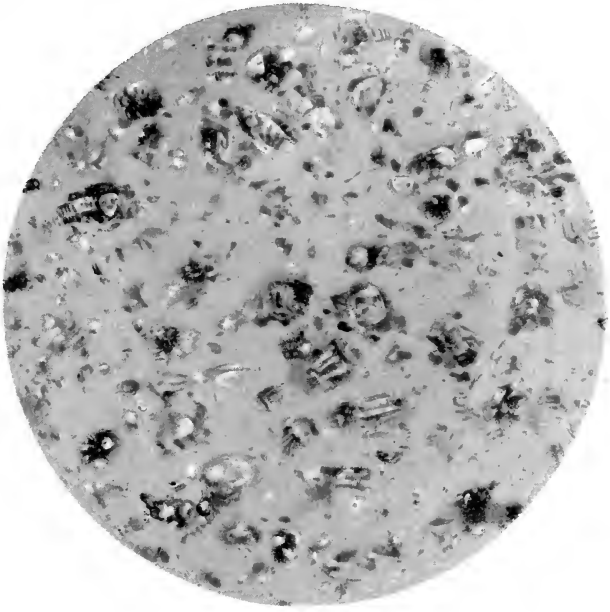

FIG. 1.—ORTHOCLASE ROCK GROUND WET IN AN AGATE MILL FOR THREE HOURS.

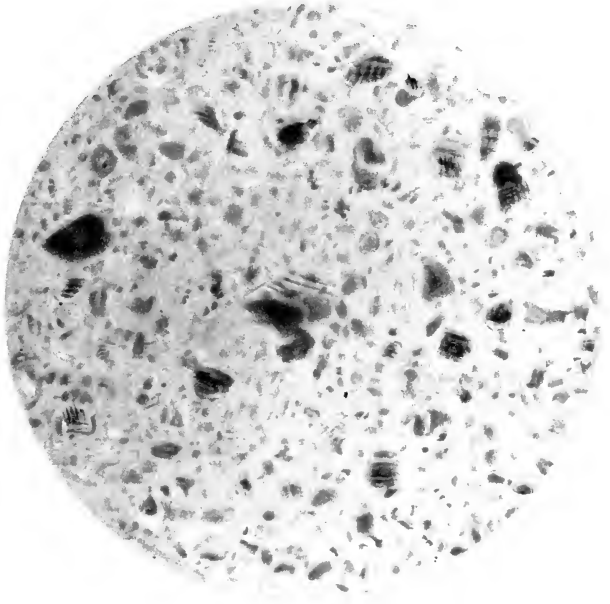

FIG. 2.—WET GROUND ORTHOCLASE STAINED WITH METHYLENE BLUE.
(ENLARGED 25 DIAMETERS).

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water. It is this reaction carried on by the action of water on this fine powder which interests us in the present inquiry. The rapidity with which water acts on the powder points to the fact that although the system, silica+alumina+lime, found in the cement clinker is in equilibrium, it becomes, on the addition of water, an unstable system, which at once begins to rearrange itself. As far as this reaction is concerned, we may be sure that if we have, for instance, tricalcic aluminate dissolved in tricalcic silicate (alit), the action of water will result in the formation of less basic compounds, such as monocalcic silicate, together with free calcium hydroxid.

A moment's reflection will show that with finely powdered glass, as in the experiments detailed above, an analogous, if not exactly similar, reaction takes place. Whether the reaction goes as far as it does in the case of cement, and whether it leads to a hydraulic set is beside the question, as, obviously, the hydraulic value must depend on the insoluble nature of calcium compounds as compared with compounds of the alkaline metals. When water acts on cement powder calcic hydroxid is at once liberated, and if the amount of water present is limited it soon becomes supersaturated with respect to lime, which crystallizes out, to be again replaced with more hydroxid until the cement is hardened, owing to the interlacing of the crystals, silicates being left of a lower degree of basicity. When water acts on glass powder, sodium hydroxid is at once liberated as the result of the hydrolysis of the sodic silicate in solution and certain insoluble silicates are left, the binding power in this case being due to the cementing value of a colloid and not to crystallization.

DISCUSSION OF PHENOLPHTHALEIN REACTION.

In view of these interesting considerations it appeared that rock powders which showed an increase in binding power after wet grinding should show an immediate and distinct reaction to indicators like phenolphthalein or litmus whenever alkali bases were present. As the laboratory of the Division of Tests has always on hand a large number of samples of all sorts of rock powders which have been fine ground both wet and dry in heavy ball mills, this point was put at once to the test. In making the qualitative test about 10-gram lots of the dry-rock powders were placed in commodious test tubes, 50 cc of water poured upon them, and a few drops of phenolphthalein indicator immediately added. Some of the results of this test are tabulated in the table.

In view of the ease with which the experiments can be repeated by anyone who wishes to do so, it has not been deemed necessary to fill any greater space with tabulated results. It is sufficient to point out that almost all fine rock powders give an immediate alkaline reaction when treated in this way, and that the color reaction is deeper after

wet grinding, while at the same time the binding power is increased. In the case of such rocks as do not contain alkaline or alkaline earth bases, this test will of course give negative results, but as these bases are usually present in the igneous rocks the samples which do not immediately respond to the phenolphthalein test are the exception rather than the rule. From the figures published by F. W. Clarke[a] for the average composition of all crystalline rocks, computed from a great number of analyses, it is found that lime and magnesia are present to the extent of about 9 per cent, while the alkaline bases, soda and potash, average about 6.5 per cent. That is to say, in 1 ton of average crystalline rock we might expect to find over 120 pounds of the soluble alkalis alone.

From the results of these qualitative tests the desire arose to follow quantitatively, if possible, the extent of the reactions carried on by water during the wet grinding process. To this end a pure orthoclase feldspar of known composition was selected and samples were ground both wet and dry. The dry ground orthoclase yielded the phenolphthalein reaction only very faintly; the wet ground sample on the other hand showed a distinct reaction. Equal weights of the two thoroughly air-dried powders were mixed with equal quantities of recently boiled and cooled distilled water thoroughly shaken for the same length of time and filtered through a Pasteur-Chamberland filter. The intention was to titrate the two filtrates with N/100 acid; therefore especial precautions were taken to insure the neutrality of the filter tube by pumping quantities of boiled water through and titrating blanks. When the two filtrates were ready for titration, however, it was somewhat disconcerting to find that in neither case were they alkaline to phenolphthalein in the cold, although before filtration they had both appeared distinctly so. On prolonged boiling the pink color appeared and required in each case about 2.5 cc of N/100 acid to discharge the color. Unfortunately, the impossibility of obtaining a definite end point in the unfiltered mixtures prevented any comparison of the relative amount of free alkali present before and after filtration.

The experiment, as described above, was tried again and again with the same sample and with various filters. A great many rock powders were then tried, and as a result of all these experiments the following fact appears: *The majority of rock powders when acted on by distilled water, whether the water has been freed from carbonic acid or not, give immediate alkaline reactions to phenolphthalein in the cold; whereas, if the water is freed from the rock powder by passage through any sort of efficient filter the alkaline reaction in the cold is either lessened or entirely inhibited in the filtrate.*

The first thought which suggests itself in the effort to find an explanation of this is that carbonic acid of the air is alone responsible

[a] U. S. Geol. Survey Bul. No. 228.

owing to the well-known extreme sensibility of phenolphthalein to this substance. It is also undoubtedly true that most filter papers have a faint acid reaction and with the Pasteur filter air is used containing its full share of carbon dioxid, under pressure. It is a very easy matter to make blanks on the filters with N/100 alkali solutions, and though these show a faint result due to the filters it is not sufficient to account for the observed differences. Again, platinum-asbestos filters produce precisely the same effect. Finally, to put the filter objection out of court, if orthoclase powder is shaken with water and then allowed to settle quite clear in a stoppered cylinder, the supernatant liquid will not give an alkaline reaction in the cold with phenolphthalein, whereas, after shaking up the sediment, a slight reaction can be obtained. Limestones and marbles behave in exactly the same way as does orthoclase powder, although the alkaline reaction is not entirely inhibited by filtration. Everyone knows that calcic carbonate is distinctly soluble even in pure water free from carbonic acid[a] and that the solution is alkaline owing to hydrolysis with an accompanying formation of calcic hydroxid.

Granting that phenolphthalein is sensitive to the small amount of carbonic acid absorbed by the alkaline solutions from the air and also that the slight acidity of some of the filters used affected the results, *it is none the less quite certain that there is some other constant cause of this phenomenon at work.* The work of other investigators substantiates this conclusion. In commenting on his own qualitative tests with phenolphthalein Clarke[b] says:

> In nearly every case the reaction was obtained at once, showing a more rapid action of water upon the silicate than had been anticipated. In some instances fading is noticed. This is doubtless due, in general, to the action of light, but in certain cases the colored solution separated in two layers, the color being wholly in the lower. Here the color was really held as a *coating on the fine solid particles*[c] and as they subsided the appearance of stratification was produced.

Following up the qualitative observations of Clarke, Steiger[d] made an attempt to study quantitatively the extent to which these reactions proceeded. Small weighed samples of finely powdered rocks and minerals were soaked in water for one month, filtered and titrated with dilute acid using methyl orange as indicator. The sort of filter used is not stated. The summing up of the results by the experimenter is very interesting. He points out that there does not seem to be any direct relation between the depth of color originally produced by phenolphthalein solution and the amounts of actual alkali found in the filtrates with methyl orange. Powders that give deep phenolphthalein

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[a] Ellms and Beneker, The estimation of carbonic acid in water, J. Am. Chem. Soc., June, 1901, **23**: 422.

[b] Loc. cit.

[c] Italics are the writer's.

[d] U. S. Geological Survey Bul. No. 167, p. 159.

reactions show but little alkali in solution and vice versa. It is further pointed out that the cause of these discrepancies remains to be ascertained.

Reduced to the simplest language, the condition of affairs may be expressed as follows: The action of water on certain rock powders is in the nature of a hydrolysis with an accompanying formation of hydroxyl ions if alkaline bases are present. After filtration or clear subsidence the number of hydroxyl ions in the clear liquid is found to be reduced.

THE COLLOID THEORY.

After this discussion it is fair to inquire if there is any theory that will account not only for the increased binding power produced in rock powders by the prolonged action of water and by wet grinding, but also for just such a phenomenon as has just been described.

Investigations carried on by Mr. L. W. Page and the writer for several years have led to the belief that the action of water on many rock powders results in the formation of colloid films on the surfaces of the particles. The word "colloid" is not altogether a satisfactory one to express this sticky, gummy condition that is being studied so much of late in relation to binding material in the various problems of road building and street paving. The word "colloid," as scientifically used, refers generally to those bodies which pass into solution in water, but which will not, while in solution, pass through a parchment diaphragm as substances in true molecular solution always will do. The word "hydrogel," given by Graham, is used to refer to the jellied colloids as they originally coagulate from the hydrosols. It does not properly describe the condition of the surface of crystalline rock particles after they have been acted on by water and thereafter air dried. Moreover, it is possible that these theories may be applied to the binding power of certain substances that have formed in an oil instead of in water, as is not unlikely to be the case with blown oils, petroleum residues, and asphalts.

Ostwald[a] says: "Colloidal substances exist in two modifications, the soluble and the coagulated or 'pectinized.'" We need another word to express this latter condition, and the word *pectoid* is truer to the Greek root ($\pi\eta\kappa\tau\acute{o}\varsigma$) than *pectinized*. The fact that this pectoid condition is superinduced on the surface of fine crystalline powders by wet grinding can be demonstrated by microscopic preparations. It has even been possible to stain the pectoid matter with methylene blue, owing to the well-known faculty of colloidal stuff of absorbing dyestuffs. Ordinary photographic prints in black and white do not suffice to show the action that has taken place. The endeavor has been made

[a] Solutions, p. 153. Translated by M. M. P. Muir. Longmans, Green & Co., New York.

to bring this out by means of illustrations colored by hand, in which the appearance observed under the microscope with polarized light is brought out as faithfully as possible. Although the colors due to the optical activity of the crystalline particles in polarized light may appear somewhat too bright in the colored plates, the results of the action of water are not in the slightest degree exaggerated. In so far as there has been failure to reproduce the exact appearance, it is because the illustrations can not do justice to what the eye easily discerns with the aid of the polarizing microscope. In making the preparations a drop of Canada balsam was placed on a glass slide, a little of the rock powder to be examined was then stirred in thoroughly with a needle, and, after warming to remove all bubbles, a cover glass was pressed down on top in the usual way.

Pl. I, fig. 1, shows the appearance of an orthoclase feldspar dust as it comes from the ball mill after having been ground *dry* for three hours.[a] A close inspection shows that although the crystals exhibit every degree of illumination as they lie in different optical planes to the direction of the ray of polarized light, each individual crystal appears with clean, clear-cut surfaces and outlines.

Pl. I, fig. 2, shows the same orthoclase powder which has been ground *wet* in the ball mill for the same length of time. Five hundred grams of crushed rock and 90 cc of distilled water were used as this mixture produced the desired pasty or doughy consistency. After the grinding process was completed the dough was thoroughly dried on the water bath, repulverized, and the microscopic slides prepared. The pectoid films and gummy material are easily seen on and among the crystals. The brown color of the pectoid matter is due to a stain which is taken up from the Canada balsam. If the mount is made with glycerin jelly the films appear colorless and almost transparent, and can only be seen with difficulty. The ability to stain readily is characteristic of this sort of matter, and serves to distinguish it from the unchanged crystalline granules.

Pl. II, fig. 1, is precisely like Pl. I, fig. 2, except that the wet grinding was done in an agate mill. It is included in order to show that the pectoid appearance is not due to iron hydroxid from the ball mill.

Pl. II, fig. 2, shows wet ground orthoclase stained with methylene blue. The dry powder is warmed with a dilute solution of the dye, thrown upon a filter and washed with distilled water. Unchanged crystalline grains will not absorb coloring matter, whereas pectoid matter is very easily stained. It is not easy to show this in an illustration as clearly as it can be seen under the microscope.

Pl. III, fig. 1, shows orthoclase dust in the finest state of subdivision

[a] The ball mill contains two chilled steel balls, which weigh 25 pounds each, and is revolved at the rate of 2,000 revolutions per hour. It has been found that rock thus ground is fine enough to pass entirely through a 0.25 mm. mesh.

that it was possible to obtain. After grinding for many hours in the mechanical agate mill, the dust was sifted by beating it through a fine, close-woven linen cloth. This sifted dust was then shaken up with air in a dry flask and the portion collected which remained the longest time in air suspension. In spite of the extreme fineness of the particles, there is no doubt of their crystalline integrity when examined under the microscope.

Pl. III, fig. 2, shows the same powder that was prepared for the preceding figure after it had been ground *wet* for one-half hour in the agate mortar and subsequently dried and repulverized. The bunching and clogging effect, due to the coagulation of the pectoid matter, is very clearly shown in this preparation, and in fact it is difficult to recognize the persistence of any crystalline particles whatever.

Pl. IV, fig. 1, is precisely the same as Pl. III, fig. 2, except that the material has been stained with methylene blue in the manner already described.

In some respects Pl. IV, fig. 2, is the most instructive illustration of the series. It represents material obtained as follows: Ordinary *wet* ground orthoclase powder, such as is shown in Pl. I, fig. 2, was thoroughly shaken with a very large excess of water and allowed to settle as much as it would during several days' standing. A certain portion of the water which still contained matter in colloid suspension was pipetted off, evaporated to complete dryness on a steam bath, and the residual materal lightly pulverized. The illustration shows quite faithfully the clumps of this matter which have taken up stain from the balsam. It is not possible to discern in this preparation the slightest indication of crystalline matter; in fact, we have what might perhaps be compared to a mineral glue.

All the evidence so far obtained points to the fact that the binding power and plasticity of rock dusts, clays, and soils are due to the formation and presence of just such matter existing either free or as cloggy films on the surface of crystalline or amorphous granules.

If suspensions in water of clays and rock powders are allowed to stand in a strong light facing a window it will be found that in some cases the sedimentation will show a tendency to collect upon the illuminated side of the glass vessel, in other cases upon the side in shadow. Quincke[a] studied this action, and spoke of such suspensions as being positively or negatively photodromic. Quincke accounts for this action as well as for the phenomenon of flocculation by supposing that the kaolin particles are coated with a thin, viscous, oily fluid layer of colloidal silicic acid. On the surface of separation of this viscous fluid from the surrounding aqueous fluid, surface tension acts. Probably changes of the surface tension will excite movements among

[a] Chem. News, 84 : 174.

the particles which lead to flocculations among the sticky particles, just as many precipitates are flocculated by mechanical agitation or boiling.

If by the influence of light more viscous film is formed on the light side of the suspended particles than on the shaded side the particles will migrate toward the light—that is, be positively photodromic. Under the contrary supposition they would go to the shaded side, or be negatively photodromic. If the viscous films contained to any extent occluded gases as well as other substances, foam cells would form, accounting not only for the indefinite suspension of the particle, but for the migratory effects under the influence of light. This phase of the subject is important and requires further investigation, as the photodromic effects are probably active on a large scale in nature.

Linder and Picton[a] have shown that when a coagulated colloidal precipitate is formed in the presence of an electrolyte a portion of the basic ions of the electrolyte is absorbed by or adsorbed on the pectoid matter in the form of the hydroxid, while the acid ions remain free in the solution. Many other investigators have checked this astonishing and most interesting fact. Whitney and Ober[b] repeated the work in the following manner: A colloidal solution of arsenious sulphid was coagulated by addition of dilute neutral solution of barium chlorid of known strength. After filtration and thorough washing a portion of the barium as hydroxid was found to have been held by the precipitate, while all of the chlorin was accounted for in the clear filtrate, which was now acid with hydrochloric acid formed by the hydrolysis. Furthermore, if the colloid precipitate was subsequently digested with a dilute solution of ammonic chlorid all the barium hydroxid was again released and passed into solution. This is an important point which will be considered in its bearing upon rock powders later on. Van Bemmelen[c] has prepared artificial hydrogels of silicic acid, aluminum silicate, calcium silicates, etc., and has found that generally when these substances form, absorption of the basic ions takes place, with an accompanying induced acidity in the clear filtrates.

It appears that in certain cases the base will be absorbed from solutions of electrolytes by pectoid substances, the acid ion remaining free in the solution. In other cases the acid will be taken and the base left, and again the whole salt will be occluded. This absorption power is in no sense of the word due to chemical combination, but seems to depend upon the fine submicroscopic porosity of the pectoid characterized by Van Bemmelen as "Struktur-Membran mit offenem

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[a] J. Chem. Soc. (Lond.), 1893, **61** : 114, 148.
[b] J. Amer. Chem. Soc., 1901, **23** : 842.
[c] Zts. anorg. Chem., 1900, **23** : 358.

Netzgewebe oder geschlossenem Wabengewebe, oder Globuliten."[a] Furthermore, there is evidence which points to the cause of the phenomenon as due to the electrostatic conditions maintained between the ions of the electrolytes and the surface charges on the particles. Coagulated precipitates of alumina and iron hydroxid will migrate to the cathode if a suitable electric current is passed through a suspension of these substances in water.[b] Silicic acid and almost all other coagulated or pectoid substances on the other hand will migrate to the anode. We may thus classify all fine materials in water suspension into positive or negative, according to their behavior in this respect. Furthermore, if positive colloids are coagulated in the presence of neutral salts the negative or acid ions will be absorbed by the precipitate while negative coagulations will absorb the positive or basic ions.

ABSORPTION POWER OF CLAYS AND ROCK POWDERS.

Certain interesting quantitative relations have been observed concerning the precipitation of coagulated colloids by electrolytes. Freundlich[c] has shown that the amount of the electrolyte used, which is necessary to precipitate a positive colloid, is in a direct ratio to the valence of the negative ions and vice versa. Although this interesting fact may seem to be very remotely related to the subject under discussion, it can be shown that it has an important bearing upon it. More than fifty years ago an English chemist, T. Way,[d] studied the absorbing power of clays and soils. This chemist noted with surprise that clays exhibited the power of absorbing the bases from certain salts dissolved in water. Also, this action was shown to be selective, certain bases being, so to speak, preferred and held in the clay substance so that they could not be washed out again. Since the time of Way the same phenomenon has been noted from time to time by other investigators, and doubtless a careful examination of much scattered scientific literature would be found to contain numerous references to the subject.

It is probable that the reason that no systemic quantitative study of these interesting absorptions has ever been made is that at first sight quantitative relations do not appear to exist. The work of Way is certainly more interesting and instructive than anything that has since appeared on the subject, and it is difficult to resist the temptation to quote liberally from his article. Two excerpts will perhaps suffice to

[a] The absortion phenomena are also carried on by other sorts of amorphous substances which are known to possess a very fine porous structure such as charcoal, boneblack, etc., but is not shared in by any sort of crystalline material. (Van Bemmelen, loc. cit., p. 322.)

[b] J. Amer. Chem. Soc., 1901, **23**: 849 et seq.

[c] Zts. physikal. Chem., 1903, **44**: 135, 151.

[d] J. Roy. Agr. Soc., 1850, **11**: 313.

FIG. 1.—ORTHOCLASE DUST IN THE FINEST STATE OF SUBDIVISION POSSIBLE

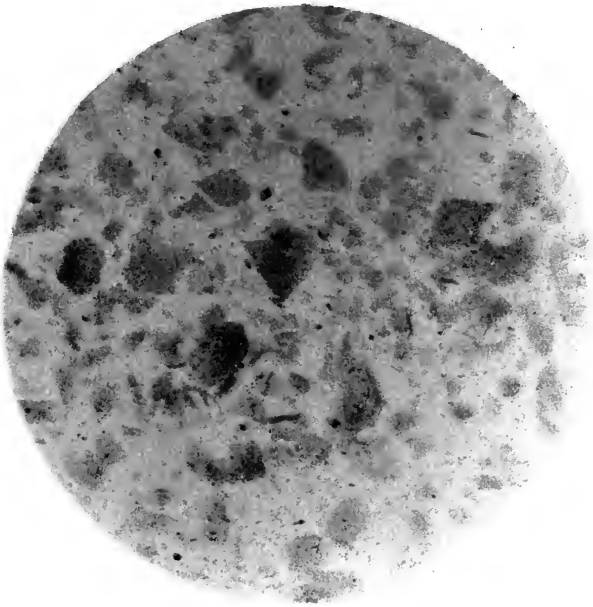

FIG. 2.—SAME POWDER AS SHOWN IN FIG. 1, GROUND, WET, DRIED, AND REPULVERISED.
(ENLARGED 25 DIAMETERS).

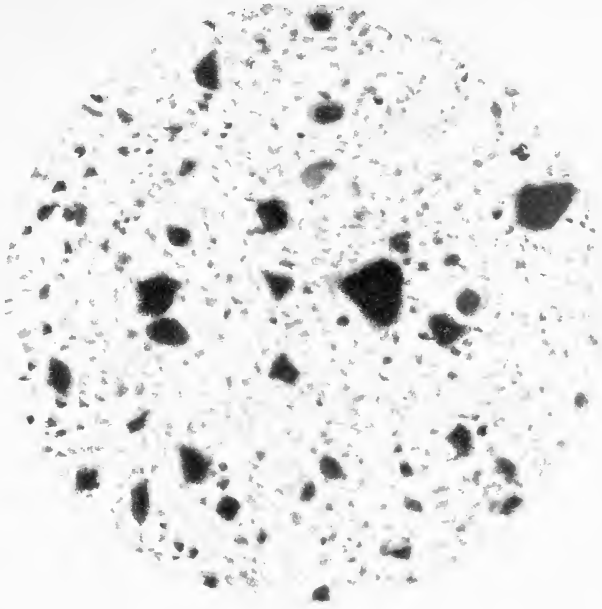

FIG. 1.—SAME POWDER AS SHOWN IN PLATE III, FIG. 2, BUT STAINED WITH METHYLENE BLUE.

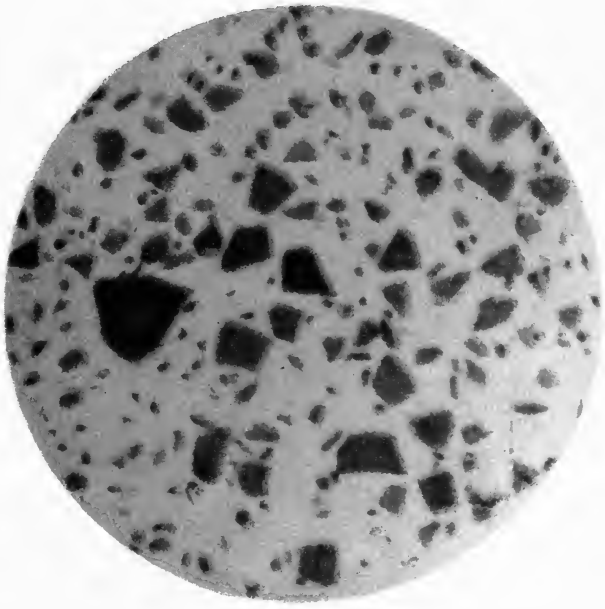

FIG. 2.—WET GROUND ORTHOCLASE POWDER, REMAINING IN SUSPENSION IN WATER AFTER SEVERAL DAYS, DRIED AND LIGHTLY PULVERIZED (ENLARGED 25 DIAMETERS).

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show the problems in agricultural chemistry that were exercising the mind of this contemporary of Liebig more than a half a century ago, and which have been to a large extent overlooked and disregarded in more modern work. On page 316, Way says:

It is to be observed that the property of sand to arrest and separate saline substances from solution is very limited in extent and requires careful arrangements to make it evident at all by experiment. It differs also fundamentally from the chemical power, which it is the object of the present paper to explain, inasmuch as the physical action of capillarity is exerted on the whole salt, whilst that we are about to describe has relation only to the alkaline or earthy base. Furthermore, the former property is only the resultant of two opposite forces, that of the surface attraction of the sand and of water for the salt. It can only, therefore, operate a condensation of the salt in relation to the strength of the solution, the salt being continually shared in given proportions between the sand and the water, so that eventually the whole is washed away. Such, however, is not the case with the compounds which are formed in the soil with solutions of different alkaline bases, for, so far as the experiments have gone, they appear to be wholly insoluble in pure water.

Again, on page 359 et seq., where the author cited is discussing a simple experiment in which 2,000 grains of white pipe clay had been boiled with 4,000 grains of a 1 per cent solution of potassium hydroxid, the mixture filtered and the filtrate analyzed, we read:

When simply digested with the solution of potash in the cold the clay absorbed 1.050 per cent of potash. When the materials are boiled together the absorption is somewhat greater or 1.1716 per cent. This, however, is not a material difference. In analytical chemistry it is usual to employ caustic potash as a means of separating silica from other substances with which it may be mixed. When boiled with potash the silica is dissolved and forms a soluble silicate of the alkali. In the experiment which has just been described we find clay, which is usually thought to contain silica in a free state, not only refusing to give up that silica to potash, but actually combining with and removing from solution the alkali. It should be understood, however, that this result is affected by the relative proportions of the two substances, since a stronger solution of potash will, even in the case of clay, dissolve out silica.

The experiment is of interest, however, in showing how powerful is the tendency of soils to form new compounds where the opportunity of gratifying that tendency may be offered them.

These observations are in essential agreement with the results of investigations which are at present being carried on in this laboratory. The tabulated and systematic presentation of the figures obtained will be reserved until more complete data have been collected, but it seems desirable, briefly, to outline here the method being followed and some of the conclusions that have already been reached. Weighed portions, usually 10-gram lots, of clays and rock powders are digested with 50 cc of tenth-normal solutions of various electrolytes. After complete subsidence or clear filtration the filtrates are analyzed.

TABLE II.—*White china clay.*

SERIES I: CLAY DIGESTED 5 MINUTES.

Amount taken.	Tenth normal solution used (50 cc).	Basic ions.				Acid ions.			
		Weight present in 50 cc solution.	Weight left in 50 cc filtrate.	Weight absorbed by 10 grams clay.	Absorption.	Weight present in 50 cc solution.	Weight left in 50 cc filtrate.	Weight absorbed by 10 grams clay.	Absorption.
Grams.		*Gram.*	*Gram.*	*Gram.*	*Per cent.*	*Gram.*	*Gram.*	*Gram.*	*Per cent.*
10.....	NH_4Cl...	0.0885	0.0801	0.0084	0.0840	0.1773	0.1789	0.0000	0.0000
10.....	$BaCl_2$....	.3425	.3110	.0315	.3150	.1773	.1767	*a*.0000	*a*.0000
10.....	$Al_2(SO_4)_3$	.1030	.0935	.0095	.0950	.4803	.4950	.0000	.0000
SERIES II: CLAY DIGESTED 15 MINUTES.									
10.....	NH_4Cl...	0.0885	0.0801	0.0084	0.0840	0.1773	0.1799	0.0000	0.0000
10.....	$BaCl_2$....	.3425	.3085	.0340	.3400	.1773	.1771	*a*.0000	*a*.0000
10.....	$Al_2(SO_4)_3$	.1030	.0958	.0072	.0720	.4803	.4999	.0000	.0000
SERIES III: CLAY DIGESTED 3 DAYS.									
10.....	NH_4Cl...	0.0885	0.0808	0.0077	0.0770	0.1773	0.1795	0.0000	0.0000
10.....	$BaCl_2$....	.3425	.3052	.0373	.3730	.1773	.1773	.0000	.0000
10.....	$Al_2(SO_4)_3$	.1030	.0955	.0075	.0750	.4803	.4840	.0000	.0000

a Within limit of experimental error.

The results which are given in Table II show conclusively that the action which takes place is rapid, as the series in which the clay was digested for three days is in essential agreement with the series in which the digestion lasted for a few minutes. An inspection of the tabulated results shows that the acid ions have not in any case been absorbed. The quantitative results which show the amount of absorption of the bases have been very carefully checked and can be accepted as practically constant for this clay with the solutions used. It is certain, however, that the figures must not be taken as indicating a definite absorption law. The barium was absorbed to a much higher degree than the aluminum, but it must be remembered that the barium chlorid solution was quite neutral, whereas it is not possible to prepare a solution of an aluminum salt of an inorganic acid that does not suffer hydrolysis and become strongly acid. Moreover, barium is not present in any form in the clay, whereas aluminum is its principal basic constituent. Undoubtedly these absorptions must be studied from the point of view of the phase law and offer an attractive and important field for research.

In view of the fact that the alkaline constituents of rock powders are to a certain extent set free by the action of water, while at the same time pectoid matter is formed, it is interesting to study the subsequent action of dilute solutions of ammonic chlorid in order to determine whether the alkaline bases can be made to pass freely into solution, as was found to be the case with colloidal precipitates.

These investigations are still in progress. The method adopted is as follows:

Definite weights (25 grams) of the rock powders are shaken up with 100 cc portions of pure water in tall cylinder glasses. Weighed portions of ammonic chlorid are then added and the cylinders thoroughly shaken, making solutions of varying but accurately known strength. After clear subsidence, or, if necessary, filtration, aliquot portions are evaporated to dryness in a weighed platinum dish, ignited to drive off all ammonium salts, and the residue weighed. After solution in boiling water the alkali present in the residue is titrated with one-hundredth normal nitric acid. The results obtained on a diabase rock powder are given in Table III.

TABLE III.—*Diabase rock powder treated with dilute solutions of ammonium chlorid*

Amount taken.	Strength of ammonium chlorid solution (100 cc used).	Weight of residue.	Amount of N/100 nitric acid used.	Remarks.
Grams.	*Per cent.*	*Gram.*	*cc.*	
25	0.000	0.0064	0.20	Does not settle.
25	.001	.0092	.80	Hardly settles at all.
25	.010	.0180	1.20	Settles partially.
25	.100	.0616	3.20	Settles clear, very rapidly.
25	1.000	.1412	6.00	Do.

It is apparent from these results that the settling or sedimenting action of the electrolytes takes place completely only after a certain amount of the salt has been added, although the amount necessary to produce complete sedimentation is very small. The weights of the residues obtained rise with the amount of the electrolyte present in the solution, as does the amount of alkali, as is shown by the number of cubic centimeters of the standard nitric acid necessary to neutralize it.

The coagulating power of dilute solutions of electrolytes on clay and kaolin suspensions has been studied by several investigators,[a] but generally the changes in concentration of the ions in the solutions after the coagulation has taken place has been overlooked.

Hardy,[b] following the work of Schulze and of Linder and Picton, concluded that the coagulative power of a salt is determined by the valence of one of its ions. This prepotent ion is either the negative or the positive ion according to whether the colloidal particles move in a positive or negative direction under the influence of the electric current. The coagulating ion is always of the opposite electric sign to the particle. This fact, that the coagulation of suspensions is a function of the valence of the active ion, seems to be established beyond all doubt. In undertaking the absorption experiments reported

[a] Franz Schulze, Pogg. Ann. 1866, **129**: 366; also, Bodländer, Gött. Nach., 1893, 267.
[b] Proc. Roy. Soc., 1900, **66**: 111.

in Table II it was supposed that the absorptions would be determined not only by the valence of the ions but by the character of the colloids that were present. If clays contain only aluminum silicate and free silica they would be entirely negative and would absorb only basic ions. If, on the other hand, they also contain, as undoubtedly many clays do, free alumina and iron hydroxid, the equilibrium would be changed and absorptions of both positive and negative ions might take place. The white china clay used in the experiments above described was a fine-grained kaolin which had the following composition:

	Per cent.
Silica (SiO_2)	56.87
Alumina (Al_2O_3)	30.20
Titanium oxid (TiO_2)	1.40
Calcium oxid (CaO)	.77
Magnesium oxid (MgO)	Trace.
Potash (K_2O)	.71
Soda (Na_2O)	.17
Phosphoric acid (P_2O_5)	.24
Water (H_2O)	9.82
Total	100.18

Since the absorptions were confined to the positive ions[a] or bases, this clay is acid or negative in character. When a clay of this kind, which contains, as this one does, small portions of the alkaline and alkaline earth bases, such as potash, soda, lime, and magnesia, is treated with dilute neutral solutions of electrolytes which contain none of these elements, such as ammonic chlorid and barium chlorid, not only do exchanges take place, the first-named bases passing to a certain extent into solution, but also the filtrates will usually be found slightly acid in reaction. This is an important point, as will presently appear. If, on the other hand, rocks such as orthoclase, containing an alkaline base (potash), are ground in a ball mill with solutions of ammonic chlorid, the resulting dough invariably smells of free ammonia at the end of the run. This is a sufficient proof in itself that the alkaline bases are set free by the action of water, even if this were not shown to be the case by the phenolphthalein test. Why, then, does not this alkali, which is set free to the extent that it can react upon ammonic chlorid and phenolphthalein, pass freely into solution?

We are in position now to apply the principles developed in the foregoing pages to the discussion of the action of water on rock powders, for which purpose, to simplify the matter, orthoclase may be taken as a type. There can be no doubt that orthoclase is, at least to

[a] It is well known that positive colloidal precipitates like ferric hydroxid absorb chlorin from solutions of neutral chlorids. Compare, Chem. Centrbl. 1905, **76**, Bd. I, 500.

a slight extent, decomposed when in the state of a fine dust or powder it is simply wet with pure water. It is not in agreement with the views of modern chemistry to suppose that the alkaline silicate is leached out, leaving the insoluble aluminum silicate like a molecular skeleton behind. It is probable that the orthoclase molecule has a definite solution pressure, and that immediately upon solution hydrolysis takes place with a deposition of the insoluble aluminum silicate in situ as colloidal film upon the surface of the particles. Wet grinding carries the action further simply because it abrades the films and permits the action of the water on fresh surfaces.

This action is not confined to orthoclase dust, but also occurs in cases of other rocks which are decomposed by water. There is good reason for believing that whenever any substance is immediately produced within a liquid in which it is insoluble it will appear and at least temporarily exist there in the so-called colloidal state. Certainly, whenever aluminum or other silicates are artificially prepared in the wet way they appear as colloidal precipitates. Granting, therefore, that the action of water on rock powders results in the formation of colloidal films on the particles, all of the observed effects that have been spoken of can be accounted for. It is perfectly apparent that if a reaction takes place in which insoluble aluminum silicate and soluble potassium silicate are coincidently formed, potash will be to a large degree held by absorption in the aluminum silicate, and there will be found an accumulation of silicic acid in solution after clear subsidence or filtration. Now, this is precisely what is found to be the case. The absorption of the basic ions by the pectoid surfaces of the particles would cause a concentration of the acid ions passing freely into solutions and thus explain the fading of the color obtained with phenolphthalein, the appearance of stratification observed by Clarke, the action of filters and sedimentation observed by the writer, and the discrepancies recorded by Steiger.

Some crystalline rock powders are very much more vigorously acted on by water than others. It is possible that this is due to the fact that rocks which contain a part of their constituents in the form of solid solutions are more easily decomposed by water, as is the case with cement and glass powder, than are the definite crystalline compounds, such as pure orthoclase.

The action of solutions of ammonic chlorid in increasing the amount of alkali which passes into solution may possibly be considered as nothing more than a simple case of metathesis, the ammonium changing place with other bases. Nevertheless, in the light of what has gone before, we are bound to consider the analogy between this action and that studied by Linder and Picton,[a] in which an arsenious sulphid

[a] Loc. cit.

precipitate which had been coagulated with barium chlorid was digested with a cold dilute ammonic-chlorid solution, after which the barium which had been absorbed was again found in the solution. The cause of such action is not at present understood, but it appears to be physical rather than chemical in its nature. It is possible that it is due in some way to the electrostatic conditions that exist between the ions and the colloidal precipitates; but, whatever the cause, if such actions take place in the disintegration of rocks, it is quite certain that it is of very great importance in the economy of nature. If, indeed, this is true, we must distinguish three kinds of alkali which will be present in wet-ground rock powders (whether ground by the processes of nature or in a laboratory mill), namely, that which goes freely into solution, that which is occluded by pectoids, and that in the rock particles which has not been acted upon. The inference is plain that in soil formation a certain proportion of the potash is continually being conserved, waiting to be made available by subsequent treatment with solutions of electrolytes.

The work of Way and other experimenters on the absorptive power of soils has been thoroughly reviewed by S. W. Johnson in the well-known book, How Crops Feed.[a] The whole review might be used as an excellent argument to support the colloid theory of rock decomposition and clay formation.

PRACTICAL APPLICATIONS.

Although it has been necessary in this paper to discuss the questions raised from the theoretical and chemical point of view, many interesting practical problems are presented, and certain effects that have long been noted, but whose causes have seemed obscure, appear to find an explanation. The clay worker has always known that kneading and working his clay bodies increases both the plasticity and binding power, and it has lately been discovered that in many cases the addition of such substances as ammonia, alum, tannic acid, etc., produces a still greater increase in these properties. In the same way the road engineer has known that wet rolling will cause a macadam surface to bind. It now appears that the more wet rolling the better, and the question arises whether the addition of suitable substances in dilute solution would be of benefit. Of the great number of different kinds of rocks used in road building only a comparatively few will furnish such a compacted surface as to be practically mud and dust free under average traffic.

A number of investigators have noted that even in moist air water is absorbed by finely powdered minerals that can not thereafter be driven off entirely except at a high temperature. This has been

[a] Orange Judd Co., New York, 1900.

generally ascribed to adsorption on the surfaces of the particles, although the improbability of such a state of things is apparent. If the hydrolytic reactions as pointed out in this paper take place, with the formation of hydrated films, it is no more remarkable that water is held in this way by certain finely powdered minerals than by precipitates of alumina or silica which are prepared in the course of an ordinary mineral analysis.

Even the finest, whitest sedimentary clays often contain small amounts of potash, and it has always been a question with what this potash was to be considered as combined when the microscope showed not the slightest trace of unkaolinized feldspar or other mineral aggregates present.

A most important problem that still awaits solution by industrial chemistry is the unlocking of the potash which is held in enormous quantities in the crystalline rocks. It is possible that by wet grinding alone or with dilute solutions of certain eloctrolytes, or by wet grinding and subsequent treatment with such solutions, the alkali can be made at least partially available. There would seem to be no doubt that analogous methods are at work in nature, in which the geological and meteorological processes are continually unlocking the plant foods from the rocks and storing them up to become slowly available for vegetation and for man.

SUMMARY.

(1) The effect of wet grinding is to increase the binding power or cementing value of rock powders, and there are indications that the addition of small amounts of suitable electrolytes to the water will still further increase the action.

(2) When water comes in contact with most rock powders immediate reactions take place, which are to a certain extent analogous to those which take place with cement and powdered glass.

(3) These reactions are shown by the alkalinity indicated by phenolphthalein, but this alkalinity is to a great degree inhibited if the solid particles are filtered out.

(4) The microscope reveals an accumulation of amorphous material of a gummy appearance largely associated with the surfaces of the crystalline particles as the action of water proceeds.

(5) Evidence is given to show that the basic ions set free associate themselves to a certain degree with the solid particles, leading to a concentration of the acid ions in the clear solution.

(6) It is shown that the behavior of rock powders after being acted on by water is similar to that of coagulated colloids artificially prepared in the laboratory, and that the formation of colloids upon the surfaces of the particles would account for the increased binding power under

the action of wet grinding. The word "pectoid" is recommended to describe the condition of the particles as being more appropriate to the connection in which it is used than the words "colloid" or "hydrogel."

(7) The absorption of the bases known to take place when certain clays are treated with dilute salt solutions is explained by means of the colloid theory, as is also their increase of binding power under the action of water and certain solutions.

(8) The possibility of rendering the potash contained in rocks available as a fertilizer is suggested.

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